Fabrication and Characterization of ZnO nanorods-based UV detectors on flexible substrate

Thesis submitted in the partial fulfillment of the requirements for the award of the degree of

MASTER OF SCIENCE
IN PHYSICS

By

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Rabi Prakash Maheswari

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CERTIFICATE

This is to certify that the project entitled "**Fabrication and Characterization of ZnO nanorods-based UV detectors on flexible substrate**", carried out by Rabi Prakash Maheswari, in partial fulfillment of the degree of Master of Science in Physics and Astronomy at National Institute of Technology, Rourkela, is a genuine work by him under my observation and supervision. The work by him is quite satisfying to the best of my knowledge.

Dr. Jyoti Prakash Kar

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Place: National Institute of Technology, Rourkela

ABSTRACT

ZnO, being a wide band gap semiconductor and due to its piezo-electric property, is the most promising material for application in optoelectronics, UV sensing devices, strain sensors, nanogenerators etc. The band gap of 3.37eV falls in the UV region, thus enabling ZnO to be used as an UV detector. This report emphasizes on using this property of ZnO to fabricate UV photo-detectors. ZnO nanorods (NRs) on a glass substrate were fabricated by hydrothermal method using Zinc nitrate and HMT as precursors. Precursor concentration was varied to see the effect on NRs. XRD, SEM characterization was carried out for structural and morphological studies. The length and the diameter of the NRs were determined by SEM. Polydimethylsilcoxane (PDMS) was drop casted on ZnO NRs. PDMS served as a flexible substrate and as a polymer matrix for ZnO NRs. The response of the ZnO NRs to UV light was investigated by analyzing the I-V plots and I-t plots for the behavior both with and without UV light. It was found that, the current increased with UV illumination.

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CHAPTER-1

1.1 Introduction

Considerable change in the physical properties of nano structured materials in contrast to their bulk counterpart made them important and widely used in science and technology. Change in the physical properties is due to the difference in characteristic structural features in of the isolated atoms and the bulk materials. At the atomic level, the change in band structure is due to 'quantum confinement' which is due to the modifications in the atomic level originating from the direct impact of the ultra-small length scale on the energy-band structure. Materials in nano dimension have their properties more influenced by surface interaction than their bulk part; an increase in surface to volume ratio ensures more effective surface phenomena. 1D nanostructures like nanowires and nanorods generally having length of 1 to 10 μm and diameter of few nanometers.

Now it comes to Why ZnO? This is due to the uniqueness and diversity of nanostructures achieved. Semiconductors have played an important role in the growth of technology over the past 60 years. In contrast to Si and Ge, ZnO, being a compound semiconductor has the benefit of direct and wide band gap (3.37 eV), which permits operation of devices at higher temperatures and reduces thermal noise of low power devices at room temperature and promising for short wavelength optoelectronic applications. ZnO also has much advantage over other compound semiconductors like GaN. Just like GaN, ZnO also has wurtzite crystal structure but in addition, ZnO is an n-type semiconductor and obtainable as bulky single crystal [1]. Zinc oxide has been widely studied since 1935 [2]. ZnO having important optical and electrical properties, can be used in many applications, such as high transmittance conductive oxide coatings

for solar cells, chemical sensor, gas sensors, UV photodetectors and acoustic wave resonators. ZnO having a band gap of 3.37 eV is transparent for visible light and operates in the UV to blue wavelengths, making it a good candidate for making LEDs and other optoelectronic purposes. The higher exciton binding energy improves the luminescence proficiency of light emission and luckily ZnO has an exciton binding energy of 60 meV. Also being amphoteric in nature, the nanostructures of ZnO can be grown on relatively low cost substrates like glass and silicon, also ZnO is quite ecofriendly. Another reason to prefer ZnO over GaN is that it responses to wet chemical etching which is extremely helpful in device fabrication. Due to the higher heat capacity, higher thermal conductivity, higher electron mobility, lower thermal expansion and lower melting temperature, ZnO is always a step ahead than other semiconductors. ZnO is a piezoelectric compound having a piezoelectric tensor greater than that of GaN and AlN, which means that ZnO is suitable for device applications in fabricating nanogenerators and strain sensors.

1.2: Properties of Zinc Oxide:

Crystal Structure	Hexagonal, Wurtzite
Lattice constant	a = 3.246 Å, c = 5.207 Å
Electron mobility	100 cm^2/vs
Molecular weight	81.38 g/mol
Density	5.67 g/cm^3
Band gap at RT	3.37 eV (direct)
Thermal conductivity	(0.6-1.0) W $cm^{-1}K^{-1}$
Refractive Index	2.00

Table 1: Properties of ZnO

ZnO is an II-VI group compound semiconductor which is obtained in the crystal structures like Wurtzite, Zincblende, and rock salt of which the wurzite phase is generally stable at room temperature. It has a hexagonal unit cell and a c/a ratio of 1.633 [3].

There is lot of scope in the growth of 1D ZnO nanostructures. Various physical and chemical methods are implemented for synthesis of ZnO nanorods. Also top-down approaches using etching are available. Among all of them, wet chemical method is relatively attractive for a number of reasons – low cost and less hazardous; even the growth take place at relatively low temperature, compatible with flexible organic substrates, and there is no need of metal catalyst also the parameters can be adjusted to effectively regulate the morphology and properties of the product [4]. In my work, I used wet chemical synthesis or the hydrothermal method to grow nanorods, some of the reasons are, it is very economic, fast way to grow nanorods and a less complicated.

UV light detection property is one of the most interesting properties of ZnO and various UV detectors are fabricated by using ZnO. ZnO NRs have much higher gain in photoconductivity and have enhanced responsivity upon UV illumination [5]. UV photo response of ZnO is based upon the adsorption and desorption of oxygen molecule [6]. ZnO NRs show a long response time in vacuum or simply they have low responsivity in vacuum. Many sensors based on ZnO have been made such as nano wire bridges [7], single nano wire devices [8] and flexible nanorods sheets [9]. For measurement these devices are exposed to air, causing surface contamination of these devices due to adsorption of other molecules and leads to degraded sensitivity [10]. UV sensitivity of ZnO is degraded by adsorption of moisture from air. Moisture together with CO_2 slowly form $Zn(CO_3)$, which roughens the surface of the NRs [11]. For ZnO NRs to be practically used as UV detector, encapsulation of them is required. PDMS, being transparent to UV is used to encapsulate NRs [12]. This silicone polymer, in addition to being UV-transparent, also has the important features like UV-sensitive, flexible and selectively gas permeable. The chemical formula for PDMS can be given as $(C_3H_6OSi)_n$.

1.3: LITERATURE SURVEY

One dimensional ZnO nanostructures are one of the most interesting research topics since mid-nineties because of their electronic, piezo-electric and opto-electronic properties. These properties of ZnO can be exploited to get UV LEDs, UV photo detectors, UV nano laser, solar cells, field effect transistors etc. Various 1D ZnO nanostructures having different morphologies can be developed by using different methods for growth [13]. The large surface to volume ratio of nanostructures is responsible for their surface properties which gives the optoelectronic properties [13]. ZnO nanostructures have been synthesized in form of nanorods (NRs), nanowires (NWs), nanotubes (NTs), nanobelts (NBs), nanosprings and nanorings etc. The properties of ZnO which caught everyone's attention are:

- direct wide band gap of 3.37 eV
- Large exciton binding energy of 60 meV
- It is piezo-electric in nature
- It is bio-safe, ecofriendly and compatible

There are many methods available to synthesize ZnO nanowires like metal organic chemical vapor deposition (MOCVD), wet chemical method, pulsed laser deposition (PLD), molecular beam epitaxy (MBE). Wet chemical methods are low cost, easily controllable, and require low temperature, so they are more preferable. The light detection and response of the ZnO NRs depends on the synthesis methods, surface properties, morphology and rate of oxygen adsorption and desorption [14].

J.G. Lu *et al.*. [15] gave an analysis by emphasizing on quasi 1D metal- oxide nanostructures. In this paper, they discussed about the various liquid phase and the vapor phase growth methods for the growth of 1D nanostructures. They also have enlisted the characteristics of some metal-oxides (ZnO, In_2O_3, TiO_2, Ga_2O_3,etc.) and also the optical, magnetic, mechanical chemical, and electrical sensing properties. Some applications

basing on the properties of these metal-oxides are also presented in this paper

S. Xu *et al.*. [16] gave a seedless method for density controlled synthesis of ZnO NRs on catalyzing the reaction by the deposition of a thin layer of Au on the substrate. They proved that precursor concentration has a role in controlling the NRs density. They also investigated Effect of growth temperature and time. They have shown that given the surface is smooth enough; NWs can also be grown on substrates like glass, metal, semiconductors and polymers, by using the same method.

Sheng Xu *et al.*. [17] Published a paper on 1D nano structures. In this paper they discussed about the wet chemical method of growth. Here they discussed about the synthetic method of preparation, various growth methods, growth mechanism corresponding to the methods, controlled growth on the substrates, the various nanostructures grown and the effect of their doping. They also provided a review for the 1D nanostructures with their functional properties in helping sensing, electronic, optoelectronic, optical, and energy harvesting devices.

In the paper, "Low temp. Wafer scale production of ZnO nano wire arrays", Lori E. Greene *et al.*. [18] have shown that the hydrothermal method for growth of NWs gives homogeneous and a dense arrangement of NWs on many substrates. They noticed the importance of seed layer of ZnO crystal for nano wire growth. Effect of time of growth on the morphology and density of NWs was also studied.

D. Kim *et al.* fabricated gas sensing device based on ZnO nanostructures, where nanostructures were grown by local heating by using the localized heat given micro heater arrays which were integrated in the device [19]. For the growth of ZnO 1D nanostructures, they used aqueous solution of Zinc nitrate, HMTA and used PEI as the precursor and these were casted onto the PDMS block over the chip [19].

C.C. Chen *et al.* have reported a mask free technique for the local synthesis of ZnO 1D nanostructures on Poly silicon nano belts and poly silicon 1D nanostructures device. It has been reported that gold nano particles as catalyst to initiate the growth of ZnO 1D

nanostructures [20].

The publication on “NW based UV Photo detectors and Optical Switches” [16], the photo response of ZnO NWs have been discussed basing on power of illumination, bias voltage and wavelength. The general principle of UV-sensing is also been described in this paper.

In the report on ZnO nanostructures, J. L. Gomez *et al.* [21] gave a detailed review on the various growth methods currently employed in industry, research. They explained the vapor–liquid– solid (VLS), chemical vapor deposition (CVD), metal– organic chemical vapor deposition (MOCVD), physical vapor deposition (PVD), and hydrothermal approach. They explained each of these methods basing upon their merits and demerits.

Hung-I Lim *et al.* in the paper Fabrication of an ultra-flexible ZnO nanogenerator for harvesting Energy from Respiration. In this paper they explained energy harvesting from h u m a n respiration. The nanowires grown on the substrate were then transferred to a PDMS substrate, which acts as a secondary substrate. J.H. Choi *et al.* [22], explained a simple but effective technique to improve the electrical properties of ZnO NWs-polymer nanocomposite.

In this thesis, we discuss about growth of ZnO NRs on a glass substrate by using hydrothermal method. Glass substrate is chosen because it is economical, easily available and can sustain moderate temperatures. ZnO seed layer could have been used for better alignment of NRs but it’s not the alignment that maters here, thus to make it more economic, seed layer is not used. PDMS is drop casted on the NRs and electrodes are deposited and device is used as an UV-detector.

CHAPTER-2

Growth Of ZnO Nanorods

2.1: Nanorods (NRs)

One dimensional nanostructures can be grown by two approaches,

a) The Top-Down approach

b) The Bottom-Up approach

In top-Down approach, large piece of the material is reduced to small pieces, while, in bottom-up approach, small constituents of that material combine to give the nanorods. ZnO NRs can be grown by PVD, Metal–Organic Chemical Vapor Deposition (MOCVD) [13], solvothermal/hydrothermal methods [23, 24], Molecular Beam Epitaxy (MBE) [23] and top down approaches (like lithography) [25]. ZnO nanostructures can mainly be synthesized by both vapor phase synthesis and solution phase synthesis.

Among all the vapor phase growth methods, The Vapor-liquid-solid (VLS) method has an advantage over others as sing this method, ZnO nanostructures on larger substrates can be grown but it works on a very high temperature of 500 ºC to 1500 ºC, and also there is a possibility of contamination due to the use of metal catalysts. MBE is very high in cost, though it can give High-quality nanorods and also the choice is substrate is limited in case of MBE.

2.1.1: Hydrothermal Method

Solution phase synthesis has an edge over the vapor phase methods as it is low cost, easy to use and a low temperature process. Both inorganic and organic substrates can be used in case of solution phase synthesis. Hydrothermal method is a special case of solution phase synthesis as it involves water as solution. In this method, the chemical

solution is heated in a sealed vessel. The NRs grown by hydrothermal method show crystalline defects due to oxygen vacancy and thus are capable of being used for many applications [26]. Hydrothermal method gives 1D NRs on substrates like glass and silicon, with high aspect ratio and is applicable for large scale production. This method provides numerous advantages due to the simple, low temperature growth and no uses of metal catalyst [27]. A seed layer is sometimes used to get better alignment of NRs. Seed-layer gives better adhesion to ZnO NRs [28]. The seed layer, as an intermediate layer, promotes vertically aligned NRs [29]. Some methods for the deposition of thin film have been discussed the last section. In this work, seed layer is not used, as the alignment is not necessary for this work. Use of the seed layer will only make it costly.

In hydrothermal method, the substrate is place in an equimolar solution of Zinc Nitrate and Hexamethylenetetramine (HMT). If the substrate has a seed layer, then it is made sure that the deposited side kept downward in the solution. Then the solution is allowed to react for 4-6 hours at 90 ºC. The milky precipitation confirms the formation of ZnO. The substrate is taken out after the desired time and rinsed with DI water to remove the loosely absorbed layer and then is allowed to dry for about half-an hour. The chemical can be explained as

$$(CH_2)_6N_4 + 6\,H_2O \longrightarrow HCHO + 4NH_3$$

$$NH_3 + H_2O \longrightarrow NH_3 \cdot H_2O$$

$$Zn^{2+} + 2\,OH^- \longrightarrow Zn(OH)_2$$

$$Zn(OH)_2 \longrightarrow ZnO + H_2O$$

2.1.2: Role of HMTA

HMTA plays an important role for the growth of nanorods. It acts as a weak base and slowly hydrolyzes to give OH^- ions, these OH^- ions helps to precipitate Zn^{2+} ions in

high pH medium. A medium of pH 7-8 is considered to be fine for the growth of ZnO NRs.

2.2: Parameters affecting the growth

There are certain parameters which affect the growth of NRs,

Precursor concentration

The average diameter of the NRs increases due to increase in concentration of the precursor solution**,** but the change in the ration of the concentration has not significant effect on the diameter of the NRs.

Growth Temperature

Growth temperature and time gives the control over the morphology and aspect ratio of NRs. For the growth of Nanostructures, always low temperature is favorable because at high temperature, the high thermal energy causes faster adsorption and re-evaporation, resulting in dense and short NRs. At low temperatures, the atoms of the vaporized reactants do not possess enough energy to diffuse through the substrate, thus they just merge and sit over the surface of the substrate and thus creating an uneven film of nuclei clusters and results in the formation of several nanostructures.

Seed Layer

Deposition of a seed layer enhances the adhesion property of the NRs and also results in a vertically aligned NRs array.

2.3: ZnO as an UV photo-detector

Several properties of ZnO,

- It has a direct wide bandgap of 3.37 eV
- Its photoluminescence band ranging from blue to yellow
- It has a high quantum yield
- Nanoparticles are stable in the aqueous solution, thus helpful in biological

applications. These properties make ZnO a promising candidate for UV-detector. Some of the ideal properties for an UV- detector can be listed as

- Fast response time
- Small reset time
- Good signal to noise ratio
- High Responsivity
- High selectivity

2.3.1: Mechanism of UV-Photodetection

ZnO, being a n-type semiconductor, oxygen molecules from the environment gets absorbed to the NRs, thus forming a depletion layer of low conductivity, near the nanorods surface. Upon UV illumination, electron-hole pairs are generated, of which, the holes move to the surface of the NRs, where negatively charged oxygen molecules are present and electrons will move to the bulk and thus by increasing the photocurrent. Some Properties which define the photo-conductivity of ZnO NRs [24, 25]

- Conductivity in response to UV illumination is high
- The Photoresponse of ZnO is linearly dependent on power of illumination
- Wavelength selectivity of ZnO is excellent
- At higher bias voltage, large photo response can be detected
- Photoresponse of ZnO depends on the condition of the ambient gas.

2.4 EXPERIMENTAL

Growth of ZnO NRs

2.4.1: Substrate Cleaning

To promote better growth of NRs and to minimize defects and impurities, Substrate must be very clean. A glass substrate was chosen and was cleaned in soap solution. Then it was treated to ultrasonic cleansing. First it was sonicated in acetone for 10 mins

followed by sonication in DI water and IPA, each for 10mins. Finally it was rinsed with DI water and then dried by spin-coating. The Cleaned substrates were kept in vacuum desiccators to avoid further contact with air.

2.4.2 Growth of ZnO NRs by hydrothermal method

To make sure that there is no contamination due to impurities present in the containers, first of all, all the beakers, wide mouth bottle, conical flask, measuring flask were cleaned by sonicating them in 5% HCl solution followed by sonicating in DI water. Nanorods were grown by global heating method. First an equimolar solution of zinc Nitrate ($Zn(NO_3)_2$,$6H_2O$) and Hexamethylenetetramine (HMT) was prepared in two separate conical flasks by dissolving each of them in 100ml of DI water. Both the solutions were thoroughly mixed in a wide mouth bottle. The cleaned glass substrate was placed inside the bottle at an angle 45 degree. The bottle was placed in a beaker containing water and an external thermometer was inserted in to the bottle. Then the setup was heated at 85 ^oC for 5 hours. The solution turned milky indicating the formation of ZnO. After 5 hrs, the sample was taken out carefully and was rinsed with DI water.

Figure 2.4.2 Hydrothermal method

2.5: Preparation of PDMS

PDMS was prepared from Sylgard 184 (Dow-corning), by adding the curing agent drop by drop to the base in a ratio 10:1. First the dimensions of the film were measured and volume of the PDMS film was calculated from the experimentally observed fact, that for 1 cm^3 of PDMS film, 0.87579 gms of PDMS (0.796 gms of base and 0.0796 gms of

curing agent) is required. The base was weighed in a container and curing agent ($1/10^{th}$) was added to it drop by drop. It was mixed thoroughly for around 15 mins so that there was a homogeneous mixing of curing agent over the whole volume. Then it was vacuum dried for 30 minutes to remove the air bubbles from the PDMS.

Figure 2.5: Sylgard 184, Dow-Corning, elastomer base and curing agent

2.6: Drop casting of PDMS on NRs

The nanorods grown on the glass substrate were transferred to the surface of PDMS by the method of drop-casting. The glass substrate with as grown NRs was placed on a clean horizontal surface and it was made sure that the glass slide doesn't move during drop-casting. The as-prepared PDMS (which was in the form of a viscous liquid) was then drop casted on the NRs. PDMS was allowed to spread uniformly over the desired area so that the thickness of the film was as desired. Then it was

Vacuum dried for 30 minutes to remove the air bubbles present inside the film and was then cured at 80 ^{o}C for 1 hour. Finally, the PDMS film containing the NRS was mechanically peeled off from the substrate.

Aluminum electrodes were deposited on the NRs/PDMS sample, by thermal evaporation by using shadow masks.

CHAPTER-3

Characterization Techniques

3.1: X-Ray Diffraction (XRD)

The physical properties of a material are subjected to the arrangement of the atoms inside the material so the determination of the crystal structure is an essential part of the structural characterization of the material. XRD gives the idea about the crystalline nature of the sample by specifying the miller indices, phase composition, crystal structure and tells whether the sample is amorphous or crystalline. X-Rays are made to fall on the sample, and the X-Rays react with the atoms of the sample. If the incident X-Rays satisfy the Bragg's diffraction condition, then the X-Rays are diffracted from the crystal. Generally, in most of the crystals, the interatomic distance is about 2-3 Å, so to characterize these samples, X-Rays are appropriate [30]. Diffracted X-Ray intensity is plotted against the scattering angle. Higher intensity implies more atoms lie in that particular plane. For certain wavelength and defined incident directions, scattered radiations from the crystalline materials give intense peaks. W.H. Bragg and L. Bragg treated the diffractions as reflection from evenly spaced planes. If monochromatic X-Rays are used, then the Bragg's law can be stated as

$$2d\sin\theta = n\lambda$$

where

n: order of diffraction

d: inter-planner spacing

θ: the angle of diffraction and

λ: the wavelength of incident radiation

From X ray diffraction we can determine

- Crystallite size (From the Scherrer's equation).
- Structure of the unit cell (Bravais lattice).
- Miller indices of the plane (h k l).
- Lattice parameters.
- Types of phases present in the sample.
- Crystalline or amorphous nature.

3.2: Scanning Electron Microscopy

Scanning electron microscopy (SEM) is used to study the morphology of the sample. An electron beam is focused on the sample to get the information about the microstructure of the sample. The atoms in the sample interact with the electrons producing various signals which contain the information about the sample's morphology. The ejected electrons gets accelerated through the high potential difference and thus gains huge momentum and thereby reduction in its wavelength. For SEM, Tungsten or Lanthanum hexaboride (LaB_6) are generally used as the filament. From the filament, electrons are emitted by heating the filament and then accelerated towards the anode. Tungsten has high m.p and lowest vapor pressure. It is heated to a high temperature to emit electrons. The electron beam generated has an energy ranging from 100 eV to 100 keV and is focused by condenser lenses [31]. Scanning coils assists raster scanning by creating vertical and horizontal deflection of the beam. Each point on the sample surface is serially scanned.

Interaction with the electrons produces secondary and back-scattered electrons and auger electrons which contains the information of the sample. The secondary electrons are of low energy, can be detected by scintillator and photomultiplier. On the other hand the back-scattered electrons are more energetic and come out from depth. The variation

of properties of material with depth can be analyzed by detecting the back-scattered electrons.

SEM provides

- Shape and size/Morphology
- Surface information/topology
- Crystallographic Information
- Composition of material by EDX.

3.3: Current-Voltage Measurement (I-V)

I-V characteristics basically deal with the measuring of current-voltage or resistance characteristics by giving a voltage/current stimulus and measuring the current/voltage respond. It is a fundamental way to characterize semiconducting materials. Measurement is carried out by depositing metal contact made on the surface of the semiconductor device. For Ohmic contacts, relation is linear but for Schottky contact, the behavior is non-linear. It enables to characterize the junction properties of semiconductors, metal- oxide-semiconductors, and metal-oxide-metals.

Figure 3.3: Keithley 6487 Piccoameter/Voltage Source

CHAPTER-4

Results and Discussions

4.1: ZnO Nanorods

4.1.1: X-Ray Diffraction

X-Ray diffraction technology was used to characterize the prepared sample. The XRD data was collected for the sample on a Rigaku Ultima IV diffractometer. The obtained data was analyzed by matching it with the standard JCPDS file, it was confirmed that ZnO NRs were grown, but the peaks for multiple directions indicate that they were randomly oriented. This was due to the absence of seeding layer.

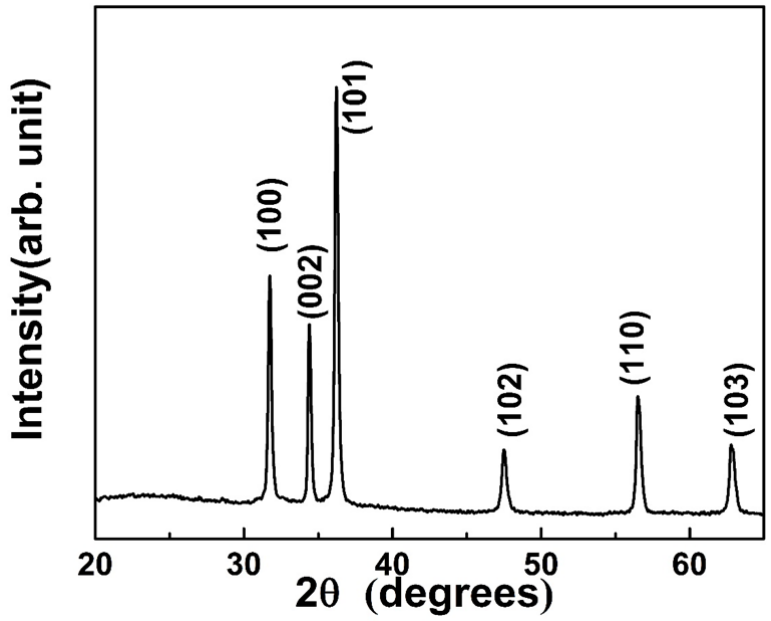
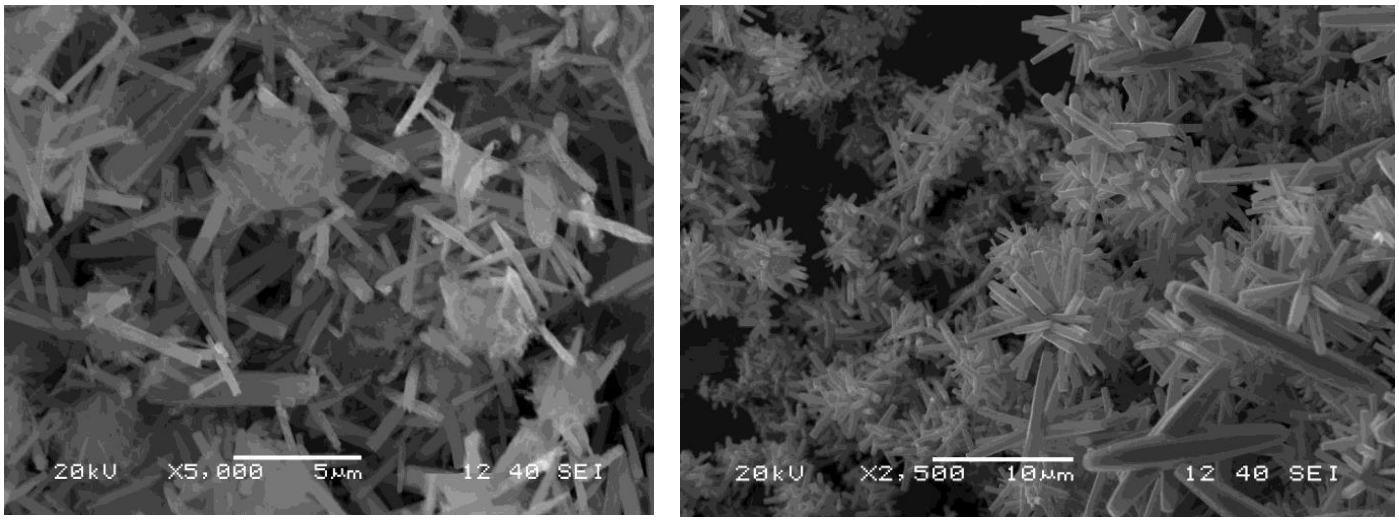


Figure 4.1: XRD Pattern of ZnO nanorods on glass substrate

4.1.2: Scanning electron microscopy

The morphology of the sample was done by scanning electron microscopy. Figures 4.1.2 (a) and (b) illustrate the images of ZnO NRs grown on glass substrate for two different concentrations. Figure (a) shows the ZnO NRs grown at 85 ^{o}C from a precursor solution of concentration 0.005 M for 4hrs. The diameter of NRs was found to be around 0.6- 0.8μm and length around 2.4 μm, because the concentration of the solution was low, so after some time, there was not much of precursor left to continue the reaction. In case of (b) time and temperature were same but the concentration was increased to 0.025 M. With increase in concentration, reaction continued for longer time and thicker rods having average diameter around 2 μm and length around 6μm were obtained. So, it was confirmed that the morphology of 1D ZnO nanorods hugely depends on the precursor concentration.



(a) (b)

Figure 4.1.2 SEM images of the 1D ZnO nanorods synthesized in aqueous solution with various molar concentrations (a) 0.005 M and (b) 0.025 M at 85 ^{0}C.

4.2: PDMS on glass:

The PDMS film on a glass substrate was characterized using X-Ray diffraction by a X-Ray diffractometer 'Rigaku Ultima IV' using a $K\alpha$ radiation, scanning the sample over $10^0<\theta<60^0$ at an operating voltage of 40 V. The XRD patterns for the PDMS films were analyzed and were matched with the JCPDS data. A broad diffuse scattering peak at around 11.7^0 was observed, which corresponds to the amorphous phase of PDMS.

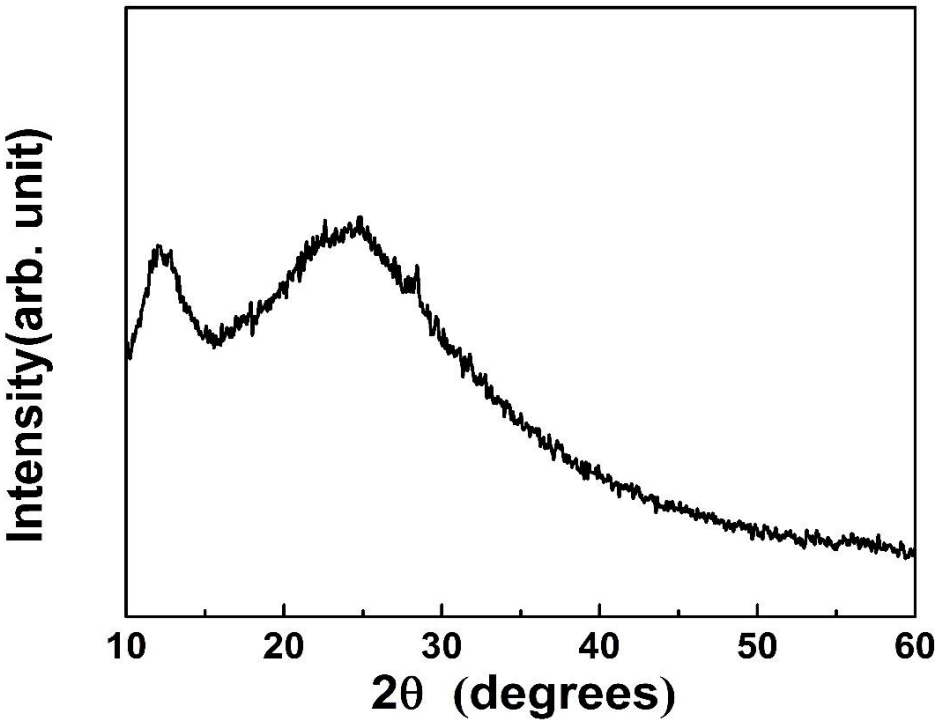


Figure 4.2: XRD Pattern of PDMS on glass substrate

4.3: ZnO NRs on PDMS

4.3.1 X-Ray diffraction:

Figure 6.3.1 illustrates the X-Ray diffraction pattern for the ZnO-PDMS hybrid device. The x-rays analysis was done by the Rigaku Ultima IV X-Ray diffractometer and the obtained data was analyzed by matchin it with the standard JCPDS data. The Crystalline nature of ZnO was confirmed from the XRD data. Multiple peaks of varying intensity were observed confirming growth of ZnO NRs in those directions. Intense peaks for (1 0 1) and (1 0 0) directions indicate that growth of nanorods was more in those directions. Also, the diffraction pattern confirms that ZnO NRs were successfully lifted off to the surface of PDMS film.

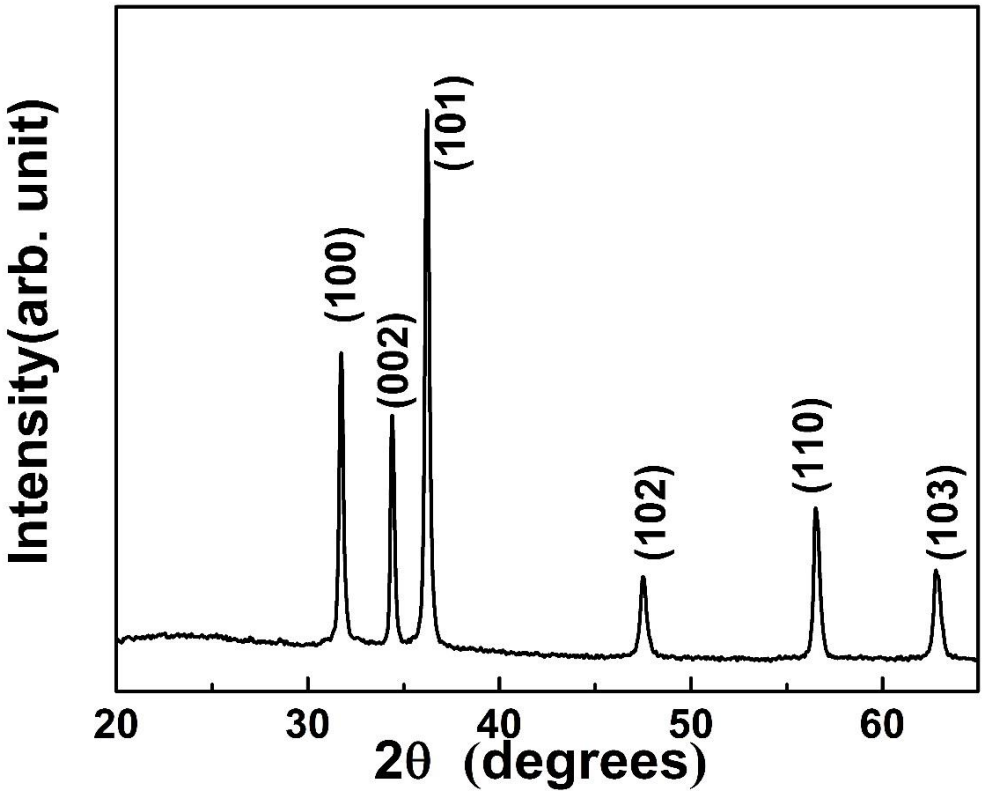


Figure 4.3.1: XRD pattern for ZnO NRs/PDMS sample

4.3.2: Microscopy:

Images of the hybrid device were captured from the optical microscope under 40x, 100 x to analyze the structure of the device.

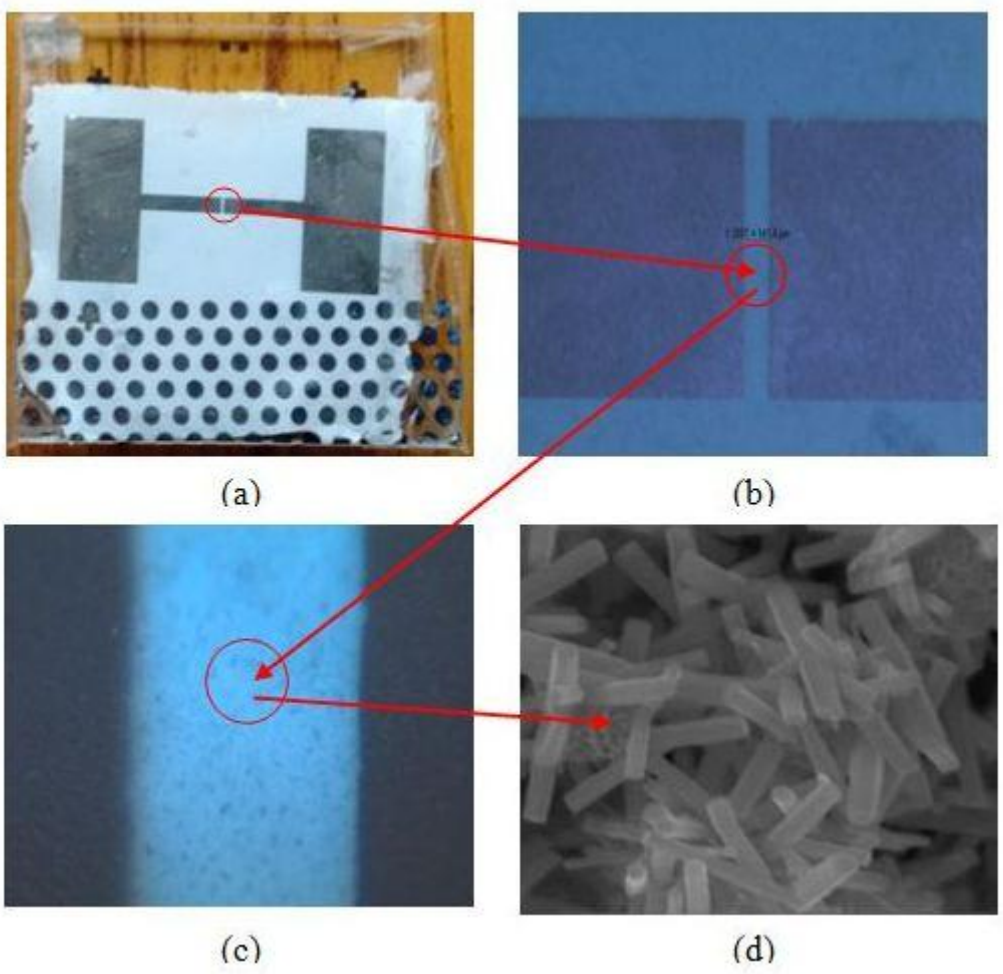


Figure 4.3.2: (a) Optical image of contact electrodes, (b) Shows the semiconducting ZnO NRs/PDMS film between the Al electrode (40X), (c) 100X magnified, (d) SEM image of ZnO NRs on PDMS films

4.3.3: I-V characteristics

The I-V characteristics are the basic characterization technique for evaluation of a semiconducting material. I-V characteristics of the NRs (grown at 0.025 M) on PDMS were measured with and without UV exposure. The I-V plots for both the cases were compared to study the response of ZnO NRs on PDMS, under UV illumination. Figure 6.3.3 shows the combined I-V graph for ZnO, both with and without UV exposure. The dark current corresponds to the I-V measurements without UV light and the photocurrent refers to the measurements with response to the UV light.

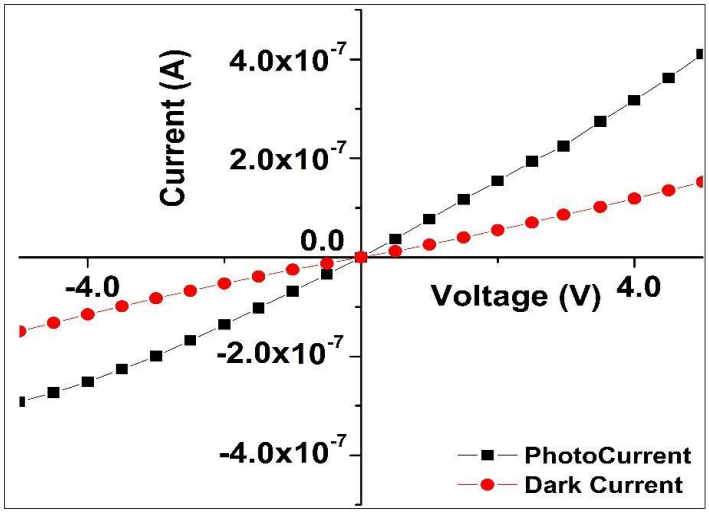


Figure 4.3.3 I-V Characteristics of Al/ZnO/PDMS

Clearly, the current is varying linearly with bias voltage and the linear relationship between current and voltage is directly implication of an ohmic contact between the semiconductor and the metal. Trend is same for both the cases, but interestingly, the slope for photocurrent is more than that for dark current. This implies photocurrent is changing rapidly with the bias voltage compared to dark current. This is due to the fact that, oxygen molecules trap free electrons and adsorb them to the surface of the NRs in absence of UV light. So there is reduced conductivity due to lack of free electrons. On UV exposure, electron-hole pairs are generated, the holes move to the surface of n-type semiconducting surface and release the electrons trapped there, thus increasing the photocurrent.

4.3.4: UV Detection

The UV detecting mechanism of ZnO NRs is based on the fact that there is a increase in the photocurrent on UV exposure. I-t relationship is analyzed for a periodic switching of UV light in every 120 seconds.

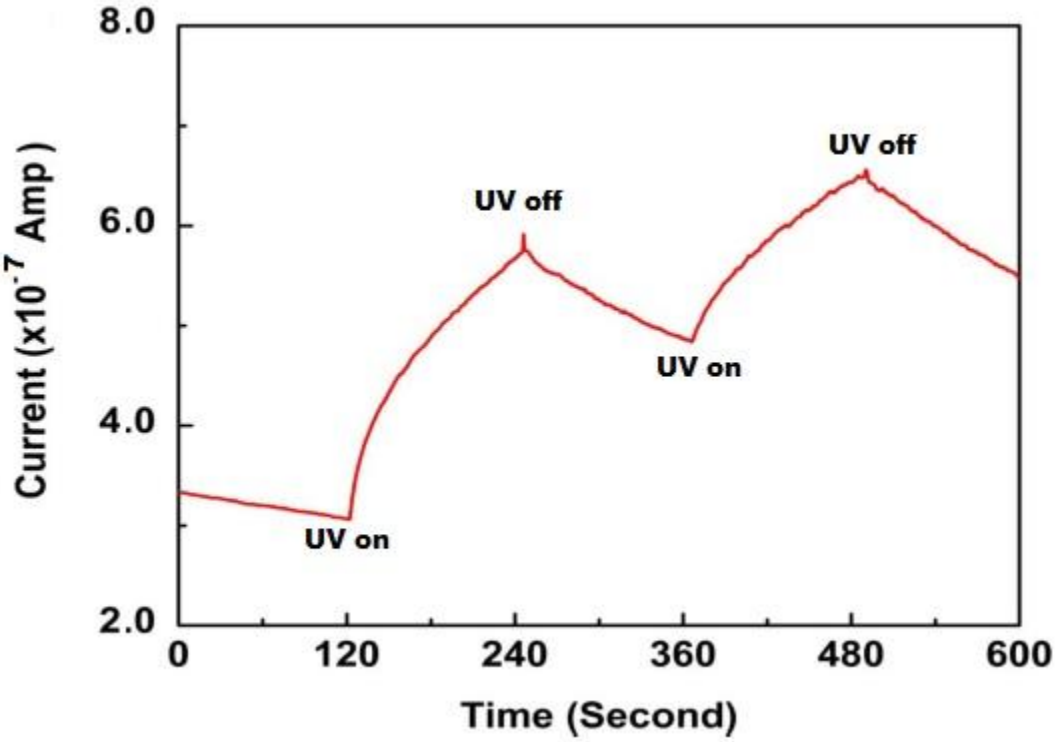


Figure 4.3.4 I-t characteristics with UV illumination.

As it can be clearly seen from the Figure 4.3.4 that for the first 120 seconds, the measurement was done without UV exposure. After 120 seconds, the UV light was switched on. A rise in current is observed at 120s and it continues to rise till 240s. At 240s, UV light is turned off, so there is decay in current but the current was observed more than that at 120s. This is because; the 120s time lap between switching off the UV and again turning it on was not enough for the oxygen molecules to trap all the electrons. The same trend continued for further periodic switching of UV light.

Conclusion

ZnO NRs were grown on glass substrate by hydrothermal method using Zinc nitrate and HMT as precursors, for different precursor concentrations. It was concluded that the concentration of precursors plays a vital role in growth of nanostructures. The crystalline nature of ZnO was confirmed by XRD analysis. The SEM images confirmed for the growth of 1D ZnO nanorods. PDMS was drop casted on ZNO NRs and the XRD analysis of the NRS on PDMS confirmed the presence of ZnO NRs on the flexible PDMS film. The wide bandgap of ZnO which corresponds to the UV range enables them to be used as an UV detector. The UV detection property of the ZnO NRs was studied by analyzing the I-V relationships, with periodic switching of UV exposure. The I-V analysis showed increase in current with UV exposure, confirming the UV detection property of ZnO NRs on flexible substrate.

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